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QUANTIFICATION OF THE EMISSIONS OF
HALOGENATED COMPOUNDS AS A FUNCTION OF
HALOGEN CONTENT OF BIOMASS BURNED IN
LABORATORY FIRES

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Quantification of the Emissions of Halogenated Compounds as a Function of Halogen Content of Biomass Burned in Laboratory Fires

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Final Report

To
USDA Forest Service
Rocky Mountain Research Station
Fire Chemistry Laboratory
Missoula, Montana 59807

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Executive Summary

The relationship between halogen (chloride, bromide) content of fuels and the emissions produced from burning these fuels was investigated. Twenty different fuels from Zambia, Montana, and the southeast U.S. were analyzed for chloride and bromide content.

These twenty fuels were then burned in small laboratory fires and the smoke was collected in stainless steel canisters. The samples were analyzed by gas chromatography with an ECD for chlorinated and brominated hydrocarbon gases. This specific method of smoke analysis was refined during this experiment.

The experimental fires and analysis of vegetation and smoke was carried out at the Fire Sciences Laboratory in Missoula, Montana.

Chloride content of the vegetation was highest in leaves and needles, in the range of 2000 to 10000 ppm. Chloride content of wood and other materials ranged from 20 to 1000 ppm. Bromine content of the vegetation was approximately one one-hundreth the concentration of chloride.

Six halocarbon gases of sufficient concentrations to be measured were identified in the canister samples- methyl chloride, methyl bromide, 1,1-dichloroethane, methylene chloride, cis-1,2-dichloroethene, and chloroform. The emission factors of each halocarbon were calculated by plotting concentration vs. CO and determining the slope of the line.

The emission factors for the six halocarbon gases were plotted vs. the chloride or bromide content of the fuel burned. The only plot that had a significant r^2 value was methyl chloride vs. chlorine vegetation content. The other halocarbon gases had low r^2 's. Chloroform and 1,1-dichloroethylene showed no linear relationship with vegetation content.

Quantification of the Emissions of Halogenated Compounds as a Function of Halogen Content of Biomass Burned in Laboratory Fires

I. Introduction

It is widely accepted that the emissions of methyl chloride, methyl bromide and methyl iodine from biomass burning affect the stratosphere as precursors to ozone layer depletion. The amount of these gases emitted from fires is related to the combustion conditions and the halogen content of the biomass burned. Preliminary research has shown that many other chlorinated compounds are produced from biomass fires in Zambia, the southeastern U.S and Alaska. These compounds include methylene-chloride, 1,1-dichloroethene, cis-1,2-dichloroethylene, 1,1,1-trichloroethane, carbontetrachloride and chloroform.

We proposed to improve the estimates of the emission factors of several halocarbons: methylene chloride, 1,1-dichloroethene, cis-1,2-dichloroethylene, 1,1,1-trichloroethane, carbontetrachloride and chloroform in addition to methyl chloride and methyl bromide by conducting a series of laboratory experiments. The accuracy of halocarbon measurements was hoped to be improved substantially, since the concentrations of these compounds in laboratory samples should be higher than the concentrations in field samples (particularly for methyl bromide and 1,1-dichloroethene).

The specific objectives for quantifying the halocarbon vegetation content and emissions were:

1. Twenty small-scale experiments were conducted at the IFSL to measure the release of chlorinated compounds from burning different types of vegetation. Vegetation, primarily conifer needles and duff materials were collected from the forest in Montana for use in these experiments. In addition a variety of vegetation previously collected from the southeast U.S and Zambia. The vegetation was burned and the emission collected in pressurized canisters. The canisters were analyzed for an array of chlorinated compounds by gas chromatography using an E.C.D detector.
2. A sub-sample of each vegetation to be burned was assayed for chloride and bromide content.
3. The results of the analysis of halogenated compounds in smoke samples and the halogen content in the vegetation were combined using statistical analysis. The emitted concentrations of halogenated compounds were correlated to the combustion efficiency for the different types of vegetation. The predictive value and relationship of vegetation halogen content to the various halogenated compounds emitted was determined using correlation and regression.

II. Methods

Vegetation Analysis

The vegetation, including litter, duff, leaves, needles, and wood was ground in a Wiley mill (1mm mesh). A 2 gram sample was extracted with 100 ml 0.1M NaNO₃, and filtered (Whatman #5 filter paper).

The chloride concentration of the extracts was determined by the thiocyanate colorimetric method (Allen, 1989). A 1 ml aliquot of the sample was mixed with reagents ferric III nonhydrate and mercuric thiocyanate solution, sodium acetate buffer, and diluted to 50 ml volume. The absorbance at 460 nm is measured after 10 minutes. Chloride standards were measured to construct a standard curve from which the chloride concentrations of the extracts and subsequently the vegetation sample was calculated.

The bromide concentration of the extracts was measured with a bromide specific ion electrode. A Fisher Scientific Accumet bromide indicating electrode with an Accumet double junction reference electrode and an Orion model 920 specific ion meter were used. Bromide standards were made from sodium bromide, from which a bromide standard curve was constructed. To each sample and standard before measurement, total adjustment buffer solution TISAB was added.

The vegetation chloride and bromide contents were calculated from the extract concentrations.

Emissions

20 fire experiments were performed, with the vegetation components from 3 regions-

Zambia- grass, leaves, litter, live woody

Southeast U.S.- live palm, gallberry, loblolly pine, litter, live woody, wood

Montana-litter, pine bark, Douglas-fir bark, Douglas-fir needles, pine needles

For each fire 200 grams of vegetation sample was spread out on a metal tray (12 by 18 inches) to a depth of 1 inch. Samples were collected in evacuated 865 ml stainless steel electropolished canisters. The collection system consisted of a Rasmussen KNF model UN 05 pump with a flow rate of 2 liters/minute. A ¼ inch stainless steel sampling line which was suspended over the sample tray with an inline 15 micron stainless steel filter leading to the pump. Downstream from the pump consisted of a pressure gauge and an adjustable pressure relief valve teed off of the stainless steel line leading to the canister. The canisters were pressurized with sample to 25 psia, the fill pressure of the canister was determined by the exhaust pressure relief valve setting.

Prior to ignition a background canister was collected. Then the vegetation was ignited at one end of the pan with a propane torch. Once the vegetation began to flame well the first canister was collected. Next a series of flaming and smoldering samples were

collected, dependent on the behavior of the fire. Generally 1 or 2 flaming samples were collected and 2 or 3 smoldering samples.

Gas Chromatography Analysis of the Canisters

Preconcentration

Halogenated compounds are cryogenically trapped and analyzed by gas chromatography (Hewlett-Packard 5890 series II) using a modified E.P.A method TO-14. The cryogenic system includes a 4' long x 1/16" o.d (0.03" i.d.) stainless steel coiled trap packed with glass beads (Supelco, 80/120 mesh), a Tylan FC-280S mass flow controller, a Setra digital pressure gauge (model 304-1), a vacuum pump (Welch, model 8905), and a Valco 6-port valve in a heated enclosure.

The trap is submerged in liquid nitrogen in a dewar at -196°C , to trap and concentrate the gases. The sample in 865 ml canister is drawn, through the flow controller and the valve, to the cold trap by an evacuated canister. The flow rate of the sample is controlled at $5\text{ ml}\cdot\text{min}^{-1}$. The volume of the sample collected is determined from the pressure increase in the evacuated canister.

After preconcentration of the sample, the valve is switched from the trap mode to desorption mode, and the trap is quickly moved from the liquid nitrogen dewar flask to a boiling water bath on a hot plate. The N_2 carrier gas of the GC then passes through the valve and the trap and returns to the GC where the sample is focused at the head of the column at -80°C .

Column and Carrier Gas

A J&W scientific DBVRX column (60 m long x 0.25 mm i.d.) is used. This column at -80°C acts as a stationary phase for focusing the compounds at the head of the column. The flow rate of the carrier gas N_2 is 1.3 ml/min with a column head pressure at 23 psi. The compounds are detected with an electron capture detector (E.C.D). A makeup of gas Ar/CH_4 with O_2 permits a high sensitivity of the E.C.D for monohalocarbons but affects the linearity of the detector. The makeup gas was at 30 psi with a flow rate of 60 ml/min, a higher flow will reduce the sensitivity of the detector.

Gas Chromatograph Conditions

Volume of the sample trapped: 100 ml
Temperatures: Detector: 350°C
 Injector: 250°C
Oven temperatures:

Initial temperature: -80 °C, hold 10 min

Temperature Program

Rate (C/min)	Final temp.(C)	Hold time (min)
30.0	0	10.00
0.5	35	0.00
50.0	200	30.00

The analytical run time is 85 min and the column is vented for 30 min, the total run time is 126 minutes.

Calibration

The retention times and concentrations of 9 compounds were determined by using standards containing 100 ppb of: methyl chloride, chloroethane, 1,1-dichloroethene, methylene-chloride, 1,2-dichloroethane, cis-1,2-dichloroethene, chloroform, 1,1,1-trichloroethane, and carbon tetrachloride. Also a 700 ppb methyl bromide standard was diluted to concentrations ranging 0.5 -20ppb. The calibration of each compound is achieved by measuring the standards at a range of concentrations to produce a standard curve. The reproducibility of the method is determined by the reproducibility of the retention time, and the ratio of the peak area to the concentration for each compound (or response factor) from multiple runs of the 100 ppb standard diluted in a range of 0.1 to 10 ppb concentrations. The dilution of the standard to obtain the concentration desired is made by mixing the standard with ultra high purity N₂ in various proportions. A canister is filled first with the standard at a set pressure using a highly accurate measurement system, and then N₂ is injected into the canister to the desired pressure, to dilute the standard to a specified concentration.

Analytical Method for CO and CO₂

Canister samples are analyzed for CO₂ and CO on a Hewlett Packard model 5890 Series II gas chromatograph. The CO₂ and CO analysis setup has a 1 ml sample loop that is filled directly from the canister. The column for this analysis is a 1/8" x 6 ft. Carbosphere (Alltech) carbon molecular sieve, with He carrier gas, 16 ml/min., subsequently passing through a methanizer, and FID at 300 C. CO and CO₂ are analyzed for in an isothermal run at 100 C.

Chromatogram data is collected and processed by Hewlett Packard ChemStation II software via a computer link to the gas chromatograph. The ChemStation software also controls the operating parameters of the gas chromatograph and does the integration of the peaks of the chromatograms. Three gas standards are analyzed with each set of samples to

construct a standard curve for each gas, based on integrated peak area, from which sample concentrations are calculated.

III. Results and Discussion

Vegetation

Results of the chloride and bromide analysis are in Table 2. For Montana vegetation, Douglas-fir needles and wood contained a high chloride content, approximately five times the chloride level in pine. Chloride and bromide levels were highest in grass and foliage, and generally progressively lower in larger diameter wood. Zambia grass and leaves are similar to Douglas-fir, in the range of 4000 ppm chloride for foliage, and slightly higher in live woody material (Table 1). These chloride and bromide levels are comparable to those found by McKenzie for similar vegetation (Table 1).

Chloride levels from Florida vegetation were also approximately 3500 ppm for palm and woody material, but lower for gallberry. Palm contained a higher concentration of bromide than most other vegetation (30.6 ppm). For the other southeast U.S. sites, LeJeune, Stewart, and Eglin, all of which are near the coast, bromide levels in all the vegetation generally ranged from 3–20 ppm. Notable exceptions are Eglin grass (78 ppm) and southeast palms (30–37 ppm).

Chloride levels in vegetation from Ft. Stewart and Camp Lejeune were lower than the other sites, ranging from 29 ppm for downed wood to 872 ppm in wire grass. Proximity to the ocean does not result in high chloride levels as might be expected. This may be related to

Table 1. Previous chloride and bromide analysis (ppm) of similar vegetation to that used in this experiment produced the following results (McKenzie, L., University of Montana, Ph.D. dissertation, 1995).

		Wood	Foliage	Bark	Litter	Duff	Humus	Soil	Grass	Dicots	Ash
Oregon moist temperate forest	Cl Br	8-10	940-120 13-1.9	51-16 3-<0.9	200-67 3.3-20	200-30 86-2.9	190-15 120-1.5	140-18 100-1.4			
Zambia miombo Shrubland	Cl Br	50 2.7	1600 11		490 3.3				1000 4.7	830 9.7	760 7.5
Zambia dambo Moist grassland	Cl Br								710 <0.9		740 1.9
Brazil tropical	Cl Br	90-120	230-30		100-66 12-20					470-1200 19-130	520- 730 4.7- 31

soil chloride levels. Chloride and bromide concentrations in vegetation from Eglin on the other hand were high for many components, greater than 8000 ppm for *Vaccinium*, live woody, and oak foliage (Table 1).

Canister Results

Of the ten halocarbon gases that were measured by gas chromatography six yielded results that could be statistically analyzed. The compound 1,2-dichloroethane could not be quantified (peak area at the limit of detection of the E.C.D.). 1,1,1-trichloroethane and carbon tetrachloride were not emitted during the fires (concentration remained at background level). The results of this experiment were therefore based on six gases: methyl chloride, methyl bromide, 1,1-dichloroethene, methylene chloride, cis-1,2-dichloroethene and chloroform. The concentrations ranges are from 1 ppb to 30 ppb for methyl chloride and chloroform; and 0.3 ppb to 5 ppb for methyl bromide, 1,1-dichloroethene, methylene chloride and cis-1,2-dichloroethene (Tables 3-5). CO concentrations ranges are from 0.5ppm (background) to 400 ppm (smoldering stage). CO₂ concentrations ranges are from 360 ppm (background) to 3000 ppm (flaming stage).

For each laboratory fire, one background canister and 4-6 sample canisters were collected. These samples were taken at various stages of the fire, from a mostly flaming phase to smoldering. The CO and CO₂ concentrations were measured first in each canister to give an indication of what halocarbon levels to expect. The halocarbon gas concentrations were plotted versus carbon monoxide concentration. Increasing carbon monoxide concentrations are an indicator of inefficient combustion and correlate highly with concentrations of hydrocarbons and other emissions. The emission factor was calculated as the slope of this linear regression, or the ratio of halogenated emission to CO. This represents an integrated ratio to CO for each compound. The coefficient of determination (r^2) is reported for each regression (Tables 3-5). This process is demonstrated with Figures 1 and 2. For each of the six gases halocarbon concentration was plotted vs. CO for each fire (vegetation type). Each point on the graph represents one canister (Figures 1 & 2). The range of values measured indicates the variation in CO and halocarbon concentration for flaming through smoldering phase samples. From each plot the emission factor for the halocarbon was the slope of the plot, or the ratio of halocarbon gas emission to CO emission. These emission factors are summarized for each gas for each vegetation type in Tables 3-5.

The coefficient of determination for each of these plots is also, summarized in Tables 3-5. Generally it was greater than .9, showing a strong linear relationship and consistent ratio of halocarbon to CO based on the chromatography results. For CO concentrations below 50 ppm, the compounds 1,1-dichloroethene and cis-1,2-dichloroethene have concentrations at the limit of detection, result in a larger measurement error and poorer linear correlation. Some chromatography measurement problems also contributed to lower correlations. For flaming samples with a CO₂ concentration greater than 4000 ppm, the chromatographic peak of methyl chloride is difficult to quantify because of overlap with hydrochloric acid.

Table 2. Chloride and bromide of vegetation from Zambia, Montana and the Southeast U.S. used as fuel for experimental fires.

Zambia Vegetation Analysis

Miombo	Br (ppm)	Cl (ppm)	Dambo	Br (ppm)	Cl (ppm)
Leaves	24.5	3899	Dead grass	10.1	1936
Wood 1/4 - 1	6.2	820	Live grass	20.8	2920
Wood 0 - 1/4	3.5	1844			
Live woody	15.5	4567			
Litter	6.1	2251			
Dead Grass	9.4	2672			
Live Grass	25.1	4094			

Montana Vegetation Analysis (Pine and Douglas Fir)

	Cl (ppm)	Br (ppm)
Ref Pine needle	1291	10.0
Litter #1	390	3.4
DF sticks #13	2158.	5.4
DFneedles#14	5823	7.1
DF bark #16	267.9	5.5
DF cones #17	334.8	11.2
Pine needle #5	863.3	7.4
Pine sticks #6	427.9	6.8
Pine bark #10	669.8	1.9
Pine cones#11	528.4	7.3

Florida Vegetation analysis

	Cl (ppm)	Br (ppm)
Live palm	3679	30.6
Gallberry	1345	1.4
Live woody	3516	7.4

South East Vegetation Analysis

Lejeune	Cl (ppm)	Br (ppm)	Eglin	Cl (ppm)	Br (ppm)	Steward	Cl (ppm)	Br (ppm)
1" - 3"	972.8	18.4	Grass	2208.8	20.4	Gallberry	257.0	0.3
1/4" - 1"	431.2	10.4	Live Woody	8125.0	12.9	Other woody	256.7	5.0
0" - 1/4"	422.3	12.0	0-1/4"	1070.3	7.3	Grass forbs	209.5	26.8
Bark	270.9	3.7	1/4 - 1"	363.6	2.8	Cones	54.0	0.1
Cones	224.1	9.2	Oak Foliage	8031.3	13.6	0-1/4" dead & down	31.8	1.2
Litter	372.5	13.3	Dead palm	4312.5	37.6	1/4-1" dead & down	29.0	2.2
Duff	359.1	12.1	Vaccinium	9156.3	29.8	Wax myrtle	141.9	17.6
Drape 1/4	400.2	12.9	Cones A1	500.0	14.0	Wire grass	871.6	23.4
			Grass, Live	2598.8	78.2	Vaccinium	658.8	0
			Vine A3	713.4	19.4			
			Dead Fern	134.1	0			
			Other Woody	1036.6	9.6			
			Dead Palmetto	311.0	0			
			Pine Foliage	1573.2	12.4			

Emission Factors versus Vegetation Chloride and Bromide Content

For each halogenated gas- methyl chloride, methyl bromide, 1,1-dichloroethene, methylene chloride, cis-1,2-dichloroethene and chloroform, the emission factor for each vegetation type versus chloride or bromide vegetation content was plotted, and r^2 and slope determined (Figures 3-8). The strongest linear relationship between halogen emission and vegetation content was found for methyl chloride, with an r^2 of .70 (Figure 3). Most of the variation from the regression line is at the low concentrations. The r^2 value for methylene chloride was much lower, .40.

For the other 2 chlorinated hydrocarbons measured, 1,1-dichloroethylene, and chloroform, no linear relationship was found (Figures 6 and 7).

For methyl bromide, a linear relationship between the methyl bromide emission factor and the bromide vegetation content was not found. This may be due partially to the low concentrations and resulting measurement error for both.

IV. Conclusion

The chloride and bromide content of the vegetation from three regions was measured. The results were comparable to previous measurements of similar vegetation. However the emission of halocarbon gases generally correlated poorly with vegetation content. This study indicates that for more complex chemical forms of halogens, emissions depend not only on the halogen concentration in the vegetation but also on other factors- the burning conditions of the fire and the type of vegetation itself. We have observed that the emission factors from these fires were dependent mainly on the vegetation type.

Therefore the prediction of a halogen emission factor depends on its concentration in the fuel, but of the burning condition and the vegetation type itself. Based on this research, we cannot predict the halogen emission factor for each type of vegetation, based only on the halogenated vegetation content.

To predict halogens emission factor of burning vegetation, a statistical analysis utilizing multiple regression might include parameters such as the halogenated vegetation content, vegetation type, and the burning conditions (fuel moisture, weather conditions). To construct such a model, more experiments are needed with varying climatic conditions, fuel moisture, loading and vegetation type.

Table 3. Laboratory Fires of Zambia Vegetation Collected in 1996

Vegetation Type	Cl content (g. Kg ⁻¹)	Br content (g. Kg ⁻¹)	Phase	number of canister	Conc range (CO, ppm)	Conc Range (CO ₂ , ppm)	Compound	Conc Range (Rx, ppb)	Ratio to CO (x10 ⁻³)	R2
wood	1.35	0.004	F+S	5	103	4872	methylchloride	21.73		
							methylenechloride	0.9	0.0092	0.99
							1,1-dichloroethene	4.5	0.041	0.78
							cis-1,2-dichloroethene	43.61	0.39	0.85
							chloroform	15	0.15	0.99
							methylbromide	3.64	0.036	0.90
wood	1.83	0.004	S	5	149	1960	methylchloride	15.65	0.10	0.92
							methylenechloride	1.2	0.0070	0.91
							1,1-dichloroethene	4.31	0.028	0.91
							cis-1,2-dichloroethene	16.46	0.104	0.95
							chloroform	15.22	0.11	0.97
							methylbromide	11	0.074	0.97
live woody	4.57	0.015	S	4	132	990	methylchloride	32	0.22	0.95
							methylenechloride	2.04	0.0068	0.97
							1,1-dichloroethene			
							cis-1,2-dichloroethene			
							chloroform	32	0.11	0.97
							methylbromide	6	0.023	0.91
leaves	3.89	0.025	S	4	88	854	methylchloride	18	0.21	0.93
							methylenechloride	1.2	0.0069	0.89
							1,1-dichloroethene			
							cis-1,2-dichloroethene			
							chloroform	11	0.069	0.69
							methylbromide			
grass	3.38	0.022	F+S	4	379	2854	methylchloride	80	0.21	0.99
							methylenechloride	8	0.0160	0.92
							1,1-dichloroethene	1.8	0.0036	0.93
							cis-1,2-dichloroethene	3.5	0.0086	0.98
							chloroform	60	0.14	0.99
							methylbromide	5	0.011	0.90
litter	2.25	0.006	S	5	200	1353	methylchloride	15	0.08	0.95
							methylenechloride	1	0.0049	0.99
							1,1-dichloroethene	3	0.013	0.92
							cis-1,2-dichloroethene	12	0.048	0.86
							chloroform	13	0.062	0.94
							methylbromide	8	0.038	0.95

Table 4. Laboratory Fires of Montana Vegetation Collected in 1999

Vegetation Type	Cl content (g. Kg ⁻¹)	Br content (g. Kg ⁻¹)	Phase	number of canister	Conc range (CO, ppm)	Conc Range (CO ₂ , ppm)	Compound	Conc Range (Rx, ppb)	Ratio to CO (x10 ⁻³)	R2
Pine-bark	0.669	0.002	F+S	8	143	946	methylchloride	8	0.092	0.90
							methylenechloride	2	0.013	0.79
							1,1-dichloroethene	1.2	0.0071	0.95
							cis-1,2-dichloroethene	3	0.0505	0.48
							chloroform	4	0.027	0.87
							methylbromide	1.5	0.0083	0.85
D.Fir-needles	5.823	0.007	F	6	76	1100	methylchloride	11	0.33	0.98
							methylenechloride	1.8	0.020	0.71
							1,1-dichloroethene			
							cis-1,2-dichloroethene	17	0.43	0.98
							chloroform	5	0.064	0.87
							methylbromide	2	0.044	0.94
D.Fir-bark	0.268	0.006	F	4	82	3185	methylchloride	35	0.47	0.98
							methylenechloride	6	0.082	0.99
							1,1-dichloroethene	1.1	0.0089	0.76
							cis-1,2-dichloroethene	18	0.21	0.97
							chloroform	2	0.02	0.91
							methylbromide	4	0.044	0.96
P.needles-litter	0.622	0.005	F	5	278	3708	methylchloride	35	0.11	0.90
							methylenechloride	3.5	0.012	0.98
							1,1-dichloroethene	4	0.060	0.89
							cis-1,2-dichloroethene	30	0.11	0.86
							chloroform	35	0.13	0.99
							methylbromide	5	0.020	0.88
D.Fir-branches	3.986	0.006	S	5	1410	9700	methylchloride			
							methylenechloride	20	0.012	0.76
							1,1-dichloroethene	5	0.0058	0.95
							cis-1,2-dichloroethene	88	0.059	0.91
							chloroform	11	0.0075	0.99
							methylbromide	12	0.0087	0.89
Pine-sticks	0.428	0.006	S	5	297	3345	methylchloride	49	0.16	0.92
							methylenechloride	1.2	0.0031	0.84
							1,1-dichloroethene	0.6	0.0020	0.96
							cis-1,2-dichloroethene	13	0.041	0.92
							chloroform	0.4	0.0034	0.95
							methylbromide	2.5	0.0075	0.95
Pine-needles	0.863	0.006	S F	4 1	195	3240	methylchloride	40	0.17	0.95
							methylenechloride	1.8	0.008	0.77
							1,1-dichloroethene	1.4	0.007	0.92
							cis-1,2-dichloroethene	45	0.24	0.98
							chloroform	16	0.079	0.83
							methylbromide	5	0.021	0.87

Table 5. Laboratory Fires of Florida and SouthEast Vegetation Collected in 1996

Vegetation Type	Cl content (g. Kg ⁻¹)	Br content (g. Kg ⁻¹)	Phase	number of canister	Conc range (CO, ppm)	Conc Range (CO ₂ , ppm)	Compound	Conc Range (Rx, ppb)	Ratio to CO (x10 ⁻³)	R2
live palm	3.68	0.031	F+S	6	337	5620	methylchloride			
							methylenechloride	40	0.015	0.94
							1,1-dichloroethene	10	0.022	0.99
							cis-1,2-dichloroethene	64	0.38	0.66
							chloroform	55	0.15	0.91
							methylbromide	25	0.069	0.95
gallbery	1.34	0.001	F	5	95	4730	methylchloride			
							methylenechloride	1.2	0.0073	0.53
							1,1-dichloroethene			
							cis-1,2-dichloroethene	14	0.12	0.89
							chloroform	2	0.017	0.92
							methylbromide	4	0.031	0.82
live woody	3.51	0.007	F+S	6	215	3692	methylchloride			
							methylenechloride	4	0.020	0.96
							1,1-dichloroethene	3	0.0104	0.88
							cis-1,2-dichloroethene	13		
							chloroform	8	0.039	0.9
							methylbromide	8	0.036	0.99
large diam. wood	0.43	0.010	F	5	90	2800	methylchloride	13	0.13	0.92
							methylenechloride	0.16	0.0022	0.99
							1,1-dichloroethene			
							cis-1,2-dichloroethene	30	0.26	0.7
							chloroform	5	0.05	0.93
							methylbromide	3.5	0.028	0.73
litter	0.47		F+S	5	37	1120	methylchloride	40	0.71	0.93
							methylenechloride	0.13	0.0028	0.7
							1,1-dichloroethene	0.3	0.0074	0.73
							cis-1,2-dichloroethene	9	0.18	0.38
							chloroform	2.3	0.043	0.87
							methylbromide	1.8	0.034	0.59
small branches	0.34	0.010	F+S	6	359	3266	methylchloride	25	0.053	0.8
							methylenechloride	0.30	0.0054	0.81
							1,1-dichloroethene	0.25	0.00054	0.81
							cis-1,2-dichloroethene	13	0.034	0.56
							chloroform	6	0.016	0.95
							methylbromide	8	0.023	0.97
loblolly	0.37	0.012	F+S	5	387	2715	methylchloride	25	0.062	0.99
							methylenechloride	0.3	0.003	0.94
							1,1-dichloroethene	3.86	0.008	0.93
							cis-1,2-dichloroethene	30	0.077	0.92
							chloroform	46	0.12	0.99
							methylbromide	30	0.078	0.99

Figure 1. Methyl chloride vs. CO for Zambia grass fire (4 canisters).

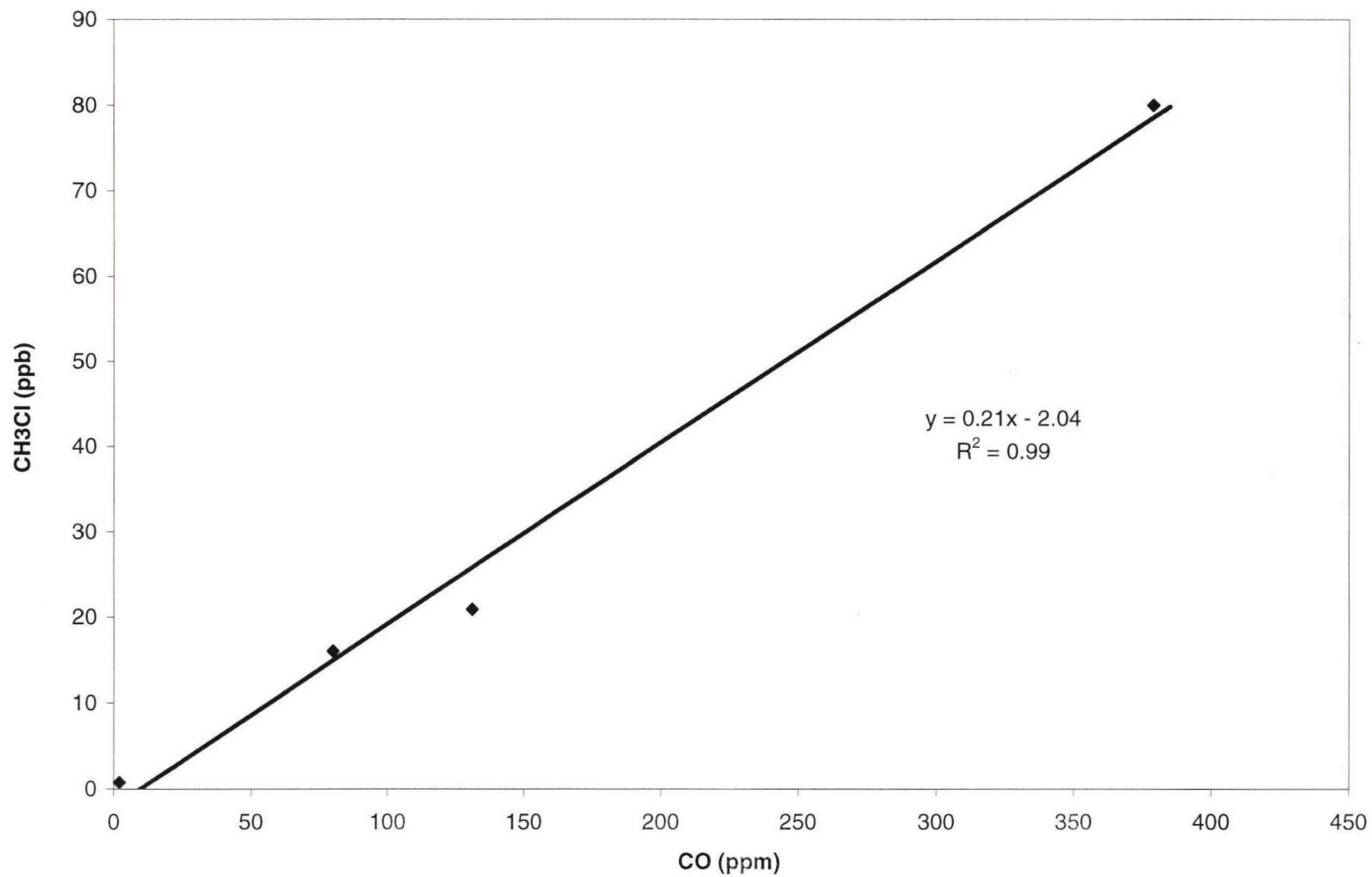
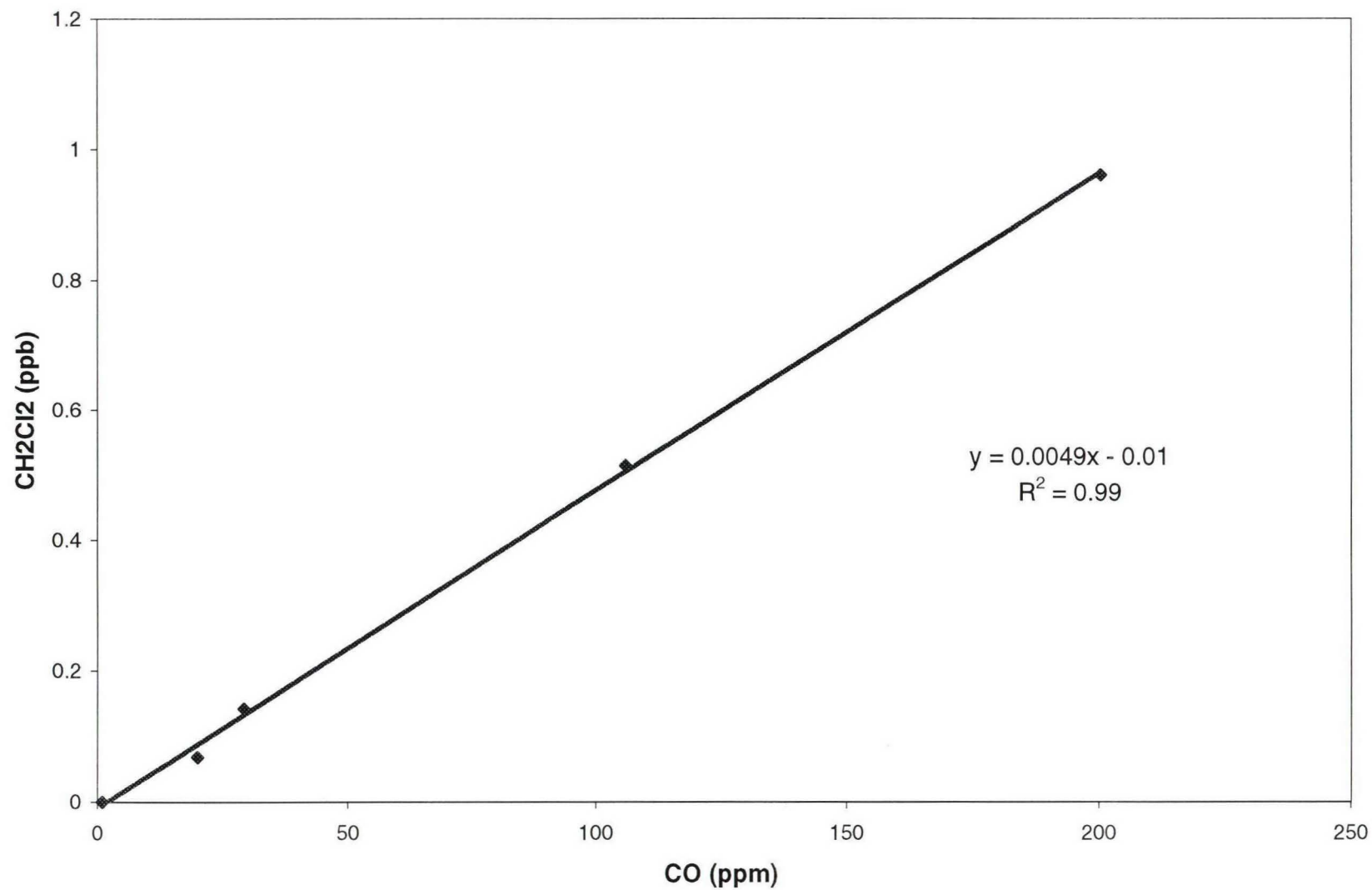
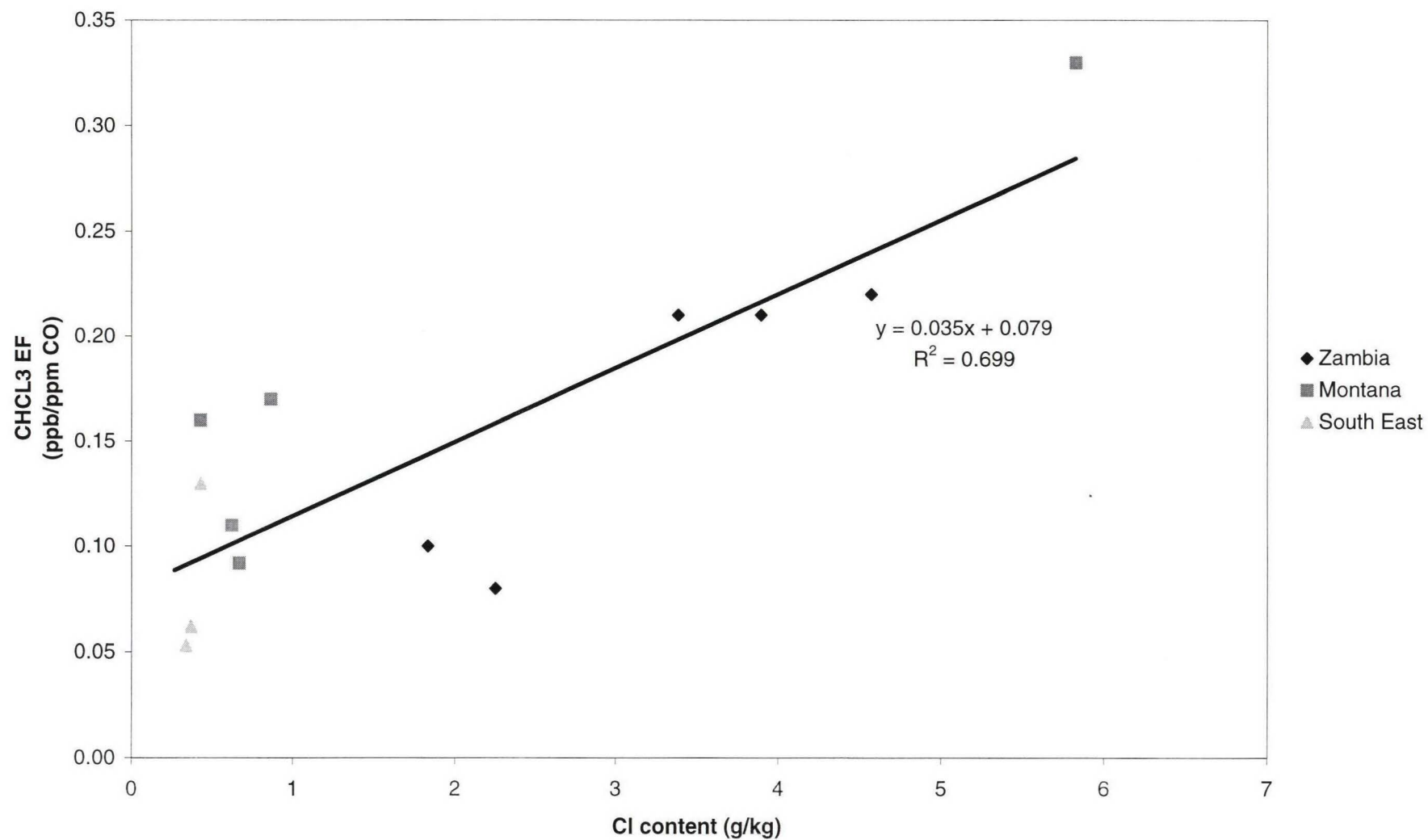


Figure 2. Methylene chloride vs. CO for Zambia litter fire experiment (5 canisters).



**Figure 3. Methyl Chloride Emission Factor
vs. Cl Vegetation Content**



**Figure 4. Methylene Chloride Emission Factor
vs. Chloride Vegetation Content**

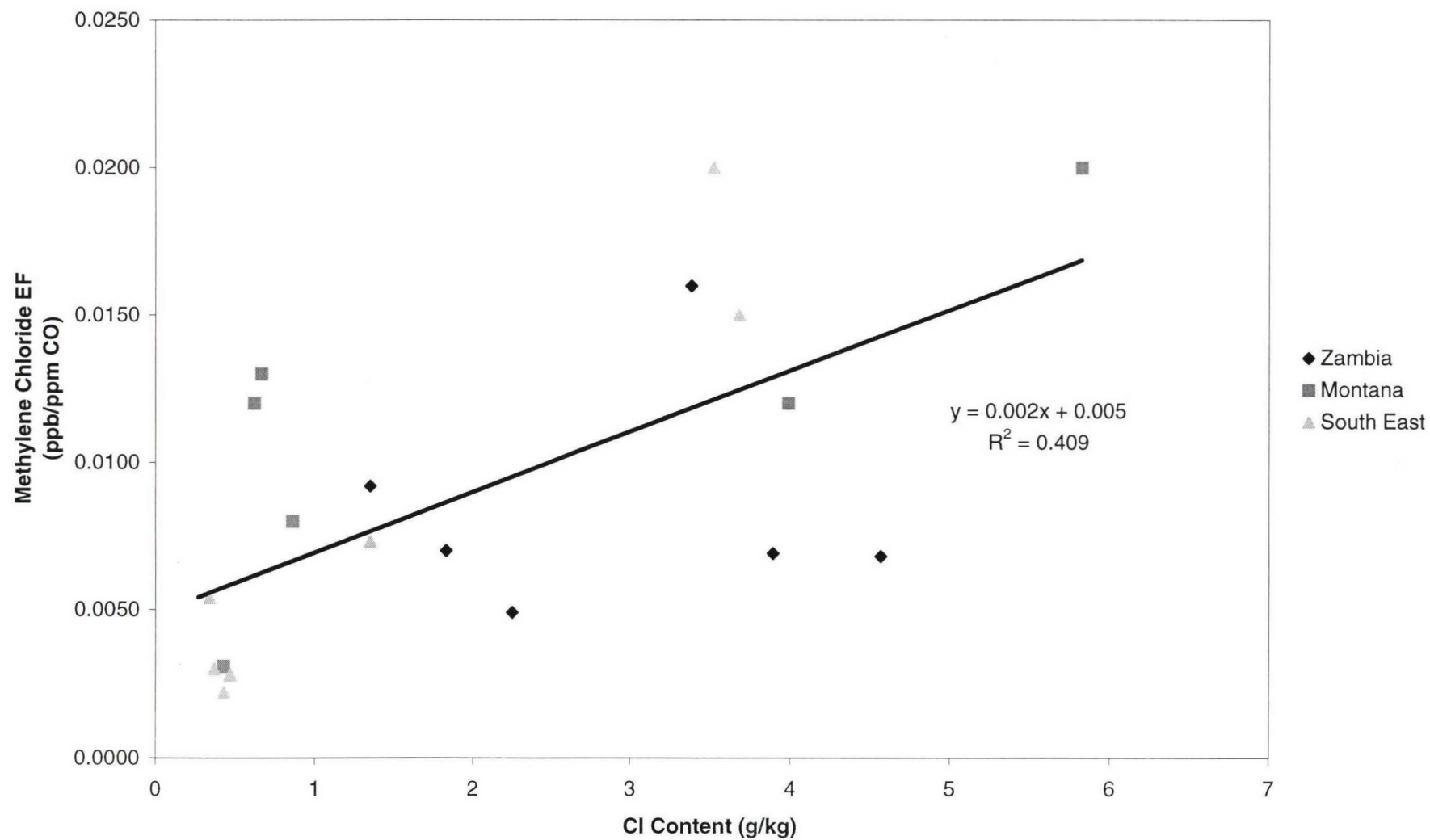
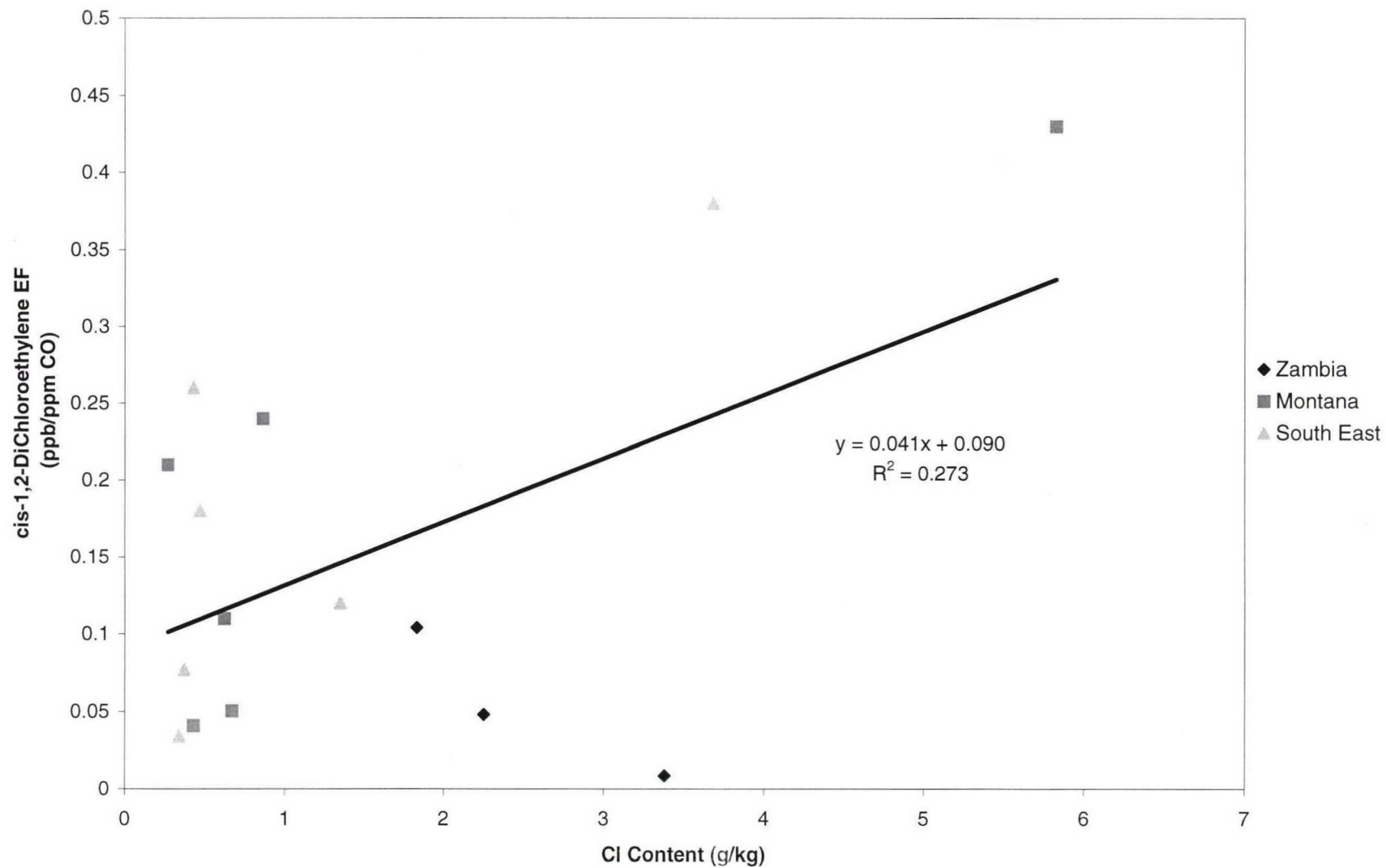
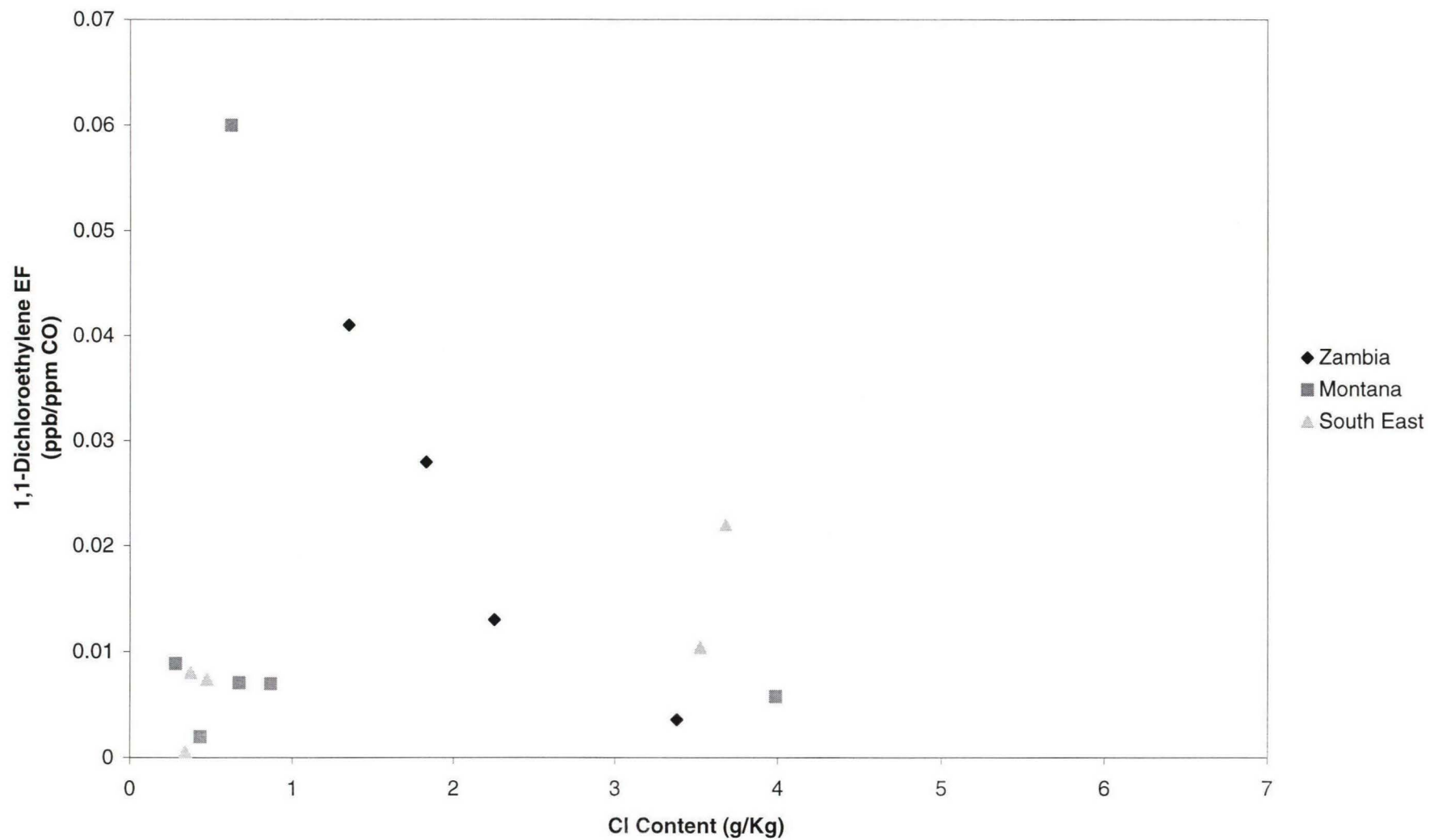


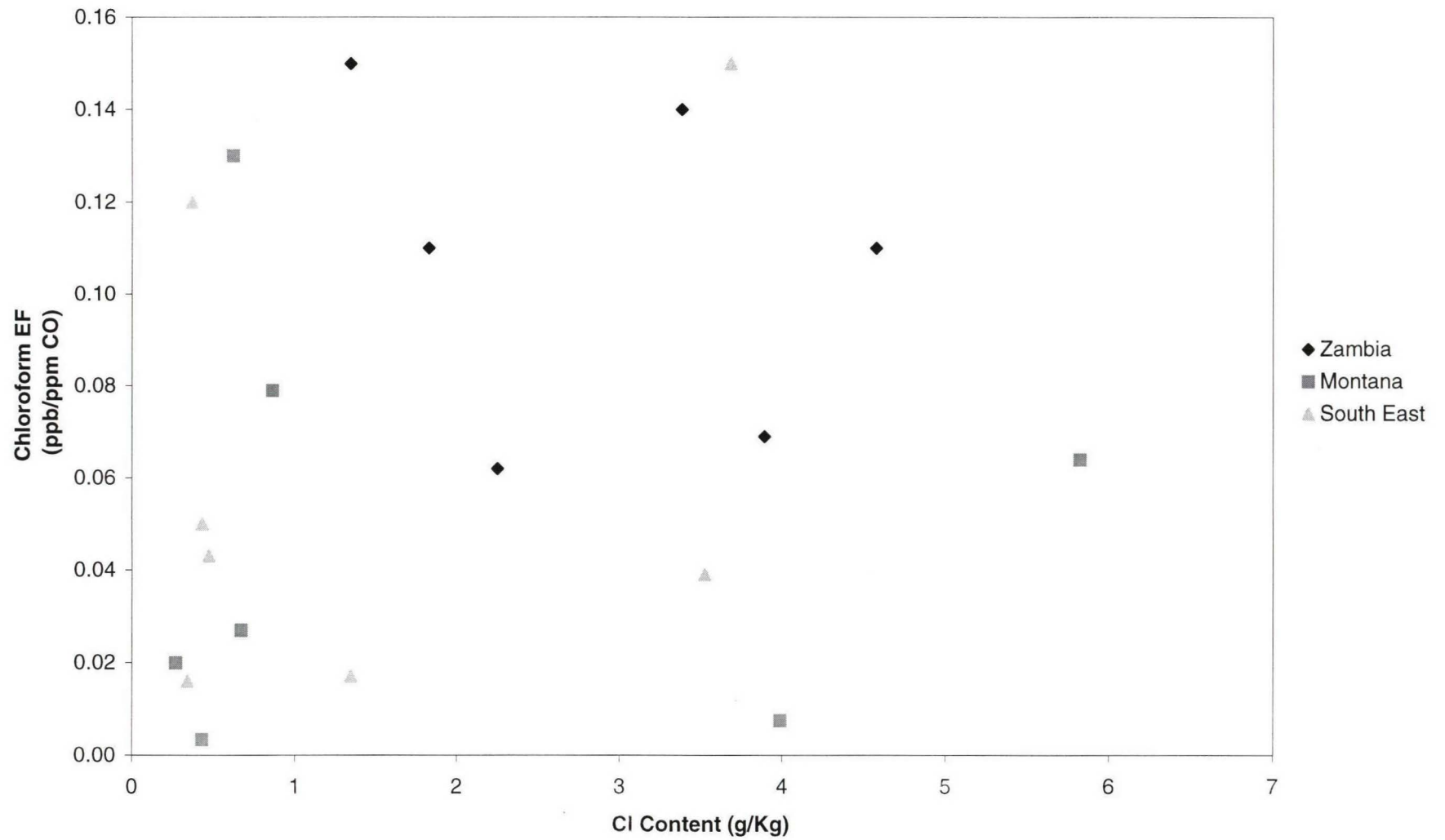
Figure 5. *cis*-1,2-DiChloroethylene Emission Factor
vs. Chloride Vegetation Content



**Figure 6. 1,1-Dichloroethylene Emission Factor
vs. Chloride Vegetation Content**



**Figure 7. Chloroform Emission Factor vs.
Cl Vegetation Content**



**Figure 8. Methyl Bromide Emission Factor
vs. Vegetation Bromide Content**

